# WORKSHOP SUMMARY Unmixing the SNCs

#### 1. INTRODUCTION

Geochemical and petrologic studies of the Martian meteorites (nicknamed the "SNCs") have proliferated in the past few years, from a wealth of new samples and the perfection of new analytical methods. An intriguing result from these studies is that the chemical and isotopic compositions of the Martian meteorites, all basalts or derived from basaltic magma, can be modeled as mixtures of a limited number of components.

These mixing components were the focus of the workshop, and the attendees brought their expertise to explore several fundamental questions about the components.

- How many mixing components can be recognized?
- Can components defined in one type of system be correlated with components in another system?
- Do the components represent physical masses of material, or chemical isotopic processes?
- How and when did the components form, i.e., become separated from the average bulk composition of Mars?
- How and when did the components come to be mixed into the SNCs?
- What are the historical, tectonic, and geological implications of the components?

Few definitive answers emerged, and finding them was not the workshop's immediate purpose. Rather, the workshop served as a forum for active researchers to present and compare their results, and perhaps as a source of inspiration. A continuing theme was the comparison of Martian geochemistry with those of other planets, especially the Moon. The issues were set against the commonly agreed results that Mars differentiated early, ~4.5 Ga, into a core and several silicate materials that could include mantle reservoirs, crust, and/or residua of a magma ocean. Several speakers discussed the idea of an early magma ocean, as many chemical systems in the Martian meteorites are closely analogous to those seen in lunar basalts.

## 2. WORKSHOP ATTENDANCE, ORGANIZATION, AND FORMAT

"Unmixing the SNCs" was held on October 11–12, 2002, at the Lunar and Planetary Institute in Houston, Texas. Fifty scientists and students attended, representing research groups from the U.S.A., Germany, Canada, Japan, and Hawai'i. The scientific sessions included 23 oral

presentations, seven of which were invited, and eight posters. The oral presentations were divided into four sessions, focused generally on radiogenic isotopes, petrologic and chemical systematics, geophysical constraints and trace element distributions, and noble gases. Ample time was provided for questions and answers, which ranged widely and engaged nearly all of the audience.

#### 3. OVERVIEW OF SCIENTIFIC PROGRAM

Abstracts associated with the workshop are available on line or in hard copy from the LPI¹. A full report of the workshop, including this summary, the program, abstracts, and list of attendees, will be available in electronic format via the LPI Web site (http://www.lpi.usra.edu/publications/meetingpubs.html). In some cases, presentations differed considerably from the abstracts, which represents the rapid pace of investigations (and reinterpretation) of the Martian meteorites.

## 3.1. Terrestrial Analogs and Thermochemistry

Several speakers from outside the Martian meteorite community were invited to the workshop to provide "real-world" analogs and constraints on the mixing processes.

Dr. Edward Ripley (Indiana University, Bloomington) spoke about chemical interactions between basaltic magmas and surrounding rocks, illustrated by his work on massive sulfide ore bodies<sup>2</sup>. Sulfur isotope ratios in these ores are characteristic of the surrounding metasediments (i.e., are characteristic of biogenic sulfate reduction) and not of mantle sulfur. Other isotopic and chemical systems are also consistent with extensive element mobility into the basalt magma, presumably mediated by aqueous fluids. Elsewhere in these deposits, fragments of the wall-rock metasediments were caught up in the magma. These fragments were partially melted by the basalts, and the melts (rich in incompatible elements) were removed from the fragments into the basalt magma. Traces of this assimilation are seen in trace element and isotopic signatures in the ore deposits and the basalt flows related to them.

Dr. C.-T. Lee (Rice University) spoke about the many complications of mantle metasomatism on Earth, both as seen in mantle samples and in basalts melted from metasomatized mantle<sup>3</sup>. Mantle material in the Earth commonly has much greater abundances of highly incompatible trace elements (e.g., La, U, Th) than would be expected from the Mg/Fe ratios of their olivine and pyroxenes. This enrichment, the metasomatism, is caused by passage of low-volume partial melts from other parts of the mantle. These melts can be silicate-rich, carbonate-rich, and/or water-rich depending on their source region and its history. Thus, metasomatized mantle can have a wide range of compositions as can basalts melted from metasomatized mantle.

Dr. A. Glazner (University of North Carolina) spoke about the thermal constraints on magma mixing<sup>4</sup>. Many interpretations of mixing and assimilation in the literature are based on

incorrect interpretations from temperature-composition phase diagrams. Phase diagrams showing enthalpy (heat content) versus composition are much more appropriate for mixing and assimilation, as they permit one to derive the correct temperature, phases present, and relative proportions of phases after mixing.

# 3.2. Isotopic Constraints

Radioisotope systematics provide the strongest evidence for component mixing in the SNC meteorites. L. Borg led off the workshop with radioisotope data that strongly suggested mixing of isotopic components in the source regions of the Martian meteorites. These systematics are comparable to those of the Moon, i.e. cumulates from the lunar magma ocean, and KREEP (the late-stage silicate magma from the magma ocean). Borg introduced an  $\epsilon^{143} Nd$  –  $\varepsilon^{142}$ Nd isochron diagram (the former derived from  $^{147}$ Sm, half life 106 Ga; the latter from  $^{146}$ Sm, half life 103Ma), on which most of the shergottite meteorites ("S" of SNC) are consistent with a single differentiation event at 4.51 Ga (and nothing between then and eruption); this is in agreement with Rb-Sr and Pb-Pb whole-rock isotopic compositions. G. Dreibus reviewed earlier isotopic and chemical evidence for the SNC meteorites, and related the meteorites to the Mars Pathfinder rock composition via their potassium contents. L. Nyquist introduced radioisotope data for the newly discovered NWA1068 shergottite, and used it and earlier data to show that the shergottites could be resolved into a mantle component and a crustal component. The crustal component is similar in some respects to the Mars Pathfinder "andesite" composition. J. Jones considered many radioisotope systems to show that the Martian meteorites and their source mantles are shockingly similar to those of the lunar basalts and their source regions; he favors a strongly layered mantle to preserve these chemical components over geological time. Treiman considered the bulk compositions of SNC meteorites as a backdrop for radioisotope systematics, and found that the effects of silicate fractionation and component mixing could (to some extent) be disentangled. At least three geochemical components can be recognized, and SNCs in a single age group seem to have similar proportions of the components. In a poster, E. Jagoutz raised the minority view that the isotopic characters of the SNCs do not indicate recent crystallization ages.

## 3.3. Constraints from Redox

Constraints on Martian basalt petrogenesis and models of the Martian interior from oxygen fugacity estimates are relatively recent<sup>5</sup>. C. Herd presented some new estimates of oxygen fugacity from mineral equilibria, and D. Musselwhite and M. McCanta presented estimates from the calibration of the Eu/Gd (or Eu/Sm) oxybarometer for Martian augites and pigeonite pyroxenes. All three methods show a large spread in oxidation states of the Martian magmas, although there are differences in the exact values of the oxygen fugacities. Herd reviewed the crustal assimilation models that have resulted from correlations between oxygen fugacity estimates and geochemical parameters, and explored in more detail implications of

oxygen fugacity for a heterogeneous mantle (e.g., as presented by Borg). Oxygen fugacity estimates require that the enriched reservoir within the mantle be oxidizing, either due to greater amounts of ferric iron, or water (likely bound up in hydrous minerals). Isotopes require that the enriched reservoir was separated from the depleted reservoir at 4.5 Ga. Therefore, the crystallization of a hydrous magma ocean is a viable model to explain the characteristics of the SNCs.

## 3.4. Constraints from Petrology

P. Hess discussed two potential models for the Martian interior using analogies with the Earth and the Moon. Continental mantle lithosphere is a potential analog because it is depleted mantle yet still garnet-bearing, it has the same age as the continental crust, and there is a decoupling of major compatible and trace incompatible elements (due to variable metasomatism). The magma ocean model is attractive because it enables heat-producing elements to be segregated, and Al can be sequestered into majorite within the lower part of the cumulate pile, thereby accounting for its depletion in the Martian basalts. J. Longhi presented many variations on partial melting models, which showed that trace elements are easy to twiddle to fit observations, but that major elements are much more difficult. Many variations on partial melting models cannot achieve the SNC parental magma compositions from the composition of the primitive upper mantle of the Earth.

D. Kring questioned the evidence for QUE 94201 being a melt (i.e., containing no cumulus minerals), since its bulk composition plots in the olivine field. However, during discussion G. McKay showed results of experiments done using the QUE 94201 bulk composition in which olivine does not crystallize at the oxygen fugacity at which the rock likely formed (~IW+1). C. Goodrich presented results of studies of melt inclusions in SaU 005 and EET 79001 lithology A showing that the melt inclusions in chromite are more representative of parental melts, and that early olivine and chromite, as well as some low-Ca pyroxene are xenocrystic. Goodrich also showed that the La/Yb ratios of SaU 005 melt inclusions (representing xenolithic magma) and groundmass are similar, whereas the La/Yb ratios of EET 79001 lithology A xenolith melt inclusions and groundmass are different. These observations are matched by differences in oxygen fugacity of the xenoliths and groundmass. Therefore it appears that melts of different mantle sources can co-exist in the same rock.

## 3.5. Geophysical Constraints

The workshop provided a unique opportunity to bring geophysicists into the discussion of the internal reservoirs of Mars. M. Parmentier presented the results of modeling involving the fractional crystallization of the entire silicate portion of Mars. Calculation of densities indicates that material at the top of the cumulate pile would be more dense than material at the bottom, and that overturn would occur. He addressed the question of the rate of overturn, which depends on

the size of the denser slab and the viscosity of the mantle. Modeling indicates that overturn could occur as quickly as 10 Ma, especially if water was present. A result of overturn is that the colder material would collect at the core-mantle boundary, and that heat loss from the core might explain an early, brief period of magnetism that is postulated from orbital magnetic measurements.

W. Kiefer, in a laudable interdisciplinary effort, used geophysical modeling of mantle convection in Mars to constrain the abundances and locations of Mars, heat-producing elements (K, Th, U). A dry Martian mantle can melt enough (and recently enough) to satisfy photogeologic constraints only if >40% of heat-producing elements are in the mantle (not in a crust). This seems consistent with the enriched component residing in the mantle. If the Martian mantle were wet, the proportion of melting increases significantly, and more of the heat-producing elements could have been extracted to a crust. Also tying geophysics and geochemistry, S. Jacobsen used the spread of initial isotope ratios for SNC meteorites with a model of mantle convection to estimate the average age of the Martian crust as 3.2–4.0 Ga (vs. ~2.0 Ga for the Earth), and the timescale of mantle mixing as ~2 Ga (vs. ~0.5 Ga in the Earth). F. Singer discussed melting models for the interiors of terrestrial planets, and argued that spindown of a satellite captured into retrograde orbit early in a planet's history could cause significant heating through tidal friction.

## 3.6. Noble Gas Isotopes

Noble gas abundances and isotope ratios in SNC meteorite have been studied intensely, but it is difficult to relate them to other radioisotope and geochemical systematics. R. Pepin gave an overview of processes that fractionate noble gas isotope ratios, emphasizing hydrodynamic escape. Pepin focused on Xe, and the difficulties in interpreting abundances of its nine isotopes. A serious problem is that Xe (even with nine isotopes) remains ambiguous — within their current precision, Xe isotope ratios can be matched by several different starting compositions with differing degrees of mass fractionation and addition of fissiogenic components. New Xe data muddles the story even further, and it appeared that Pepin's main argument was that data from the SNCs was too equivocal, and that we need to get a direct sample of the Martian atmosphere! As outlined by T. Swindle, current theories also do not explain details of Xe isotope data in the nakhlites and ALHA84001. Whereas most of the SNC data falls on a mixing line in <sup>132</sup>Xe/<sup>129</sup>Xe vs. Kr/Xe space between Martian atmosphere and Chassigny (thought to be representative of Martian interior), other data falls between Chassigny and the Nakhlites/ ALH84001, at lower Kr/Xe for a given <sup>132</sup>Xe/<sup>129</sup>Xe ratio. Available explanations for these effects are inadequate, including involving aqueous alteration, adsorption of gases on soil and subsequent incorporation into the magma, shock effects, the involvement of clathrates, and even the season or latitude at which Nakhla and ALH84001 incorporated the gas! R. Mohapatra presented noble gas data on SNC meteorites found in hot deserts, which show an additional

complication. Several of these SNCs contain a component of elementally fractionated Earth air — yet another pitfall in noble gas geochemistry.

#### 4. OVERALL COMMENTS AND LESSONS LEARNED

The format of the workshop — short presentations followed by equal (or greater) time for discussion — worked well and led to probing, interdisciplinary discussions. These discussions would have been difficult at larger, more structured meetings. For example, geophysical models of early Mars differentiation provided mechanisms for petrologists and geochemists to explain the formation of different internal reservoirs, and to speculate on where these reservoirs might be sited. Conversely, geophysicists could constrain their models by the petrologic and geochemical observations. The participation of invited speakers from the non-SNC community provided some well needed "ground truth", in the form of descriptions of processes that occur on the Earth that may be applicable to Mars. Such insight is important for a community that spends so much of its time analyzing meteoritic samples with no geologic context!

The workshop served to improve the understanding of the various aspects of the SNCs within the community, and to raise questions that can guide future research. For example, the magma ocean model was invoked repeatedly as an explanation of the internal differentiation of Mars. How well does this model explain all of the trace element variations? Do the non-lithophile element distributions tell a different story? The nakhlite source appears to be distinct from the shergottites. Does this require an entirely separate mantle reservoir from the shergottite-like mantle that has been metasomatized, or assimilation of a different type of crustal reservoir?

Finally, J. Delaney raised the issue of relevance to NASA's Mars exploration program. The workshop considered geochemical reservoirs, focusing deeper and deeper into Mars' mantle and into its earliest differentiation. Yet, future Mars missions will have access to, and investigate in detail, the Martian surface and near subsurface. How is our work relevant to the Mars exploration program? Delaney suggested a need to examine post-crystallization processes that affected the SNCs (including shock, metamorphism, alteration, and weathering) in the context of future spacecraft missions. If nothing else, workshops like "Unmixing the SNCs" provide a baseline for studies of Martian surface processes, be they *in situ* investigations or analyses of returned samples.

#### 5. ACKNOWLEDGMENTS

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#### 6. REFERENCES

- <sup>1</sup> Treiman A. H. and Herd C. D. K. eds. (2002) *Unmixing the SNCs: Chemical, Isotopic, and Petrologic Components of Martian Meteorites*. LPI Contribution No. 1134,. Lunar and Planetary Institute, Houston (Available on line at www.lpi.usra.edu/meetings/sncs2002/pdf/program.pdf).
- <sup>2</sup> Ripley E. M., Park Y. R., Lambert D. D., and Frick L. R. (2002) Re-Os isotopic variations in carbonaceous pelites hosting the Duluth Complex: Implications for metamorphic and metasomatic processes associated with mafic magma chambers: *Geochim. Cosmochim. Acta*, .
  - Ripley E. M., Park Y. R., Li C., and Naldrett A. J. (1999) Sulfur and oxygen isotopic evidence of country rock contamination in the Voisey's Bay Ni-Cu-Co deposit, Labrador, Canada. *Lithos* **47**, 53-68.
  - Park Y. R., Ripley E. M., Severson M. J., and Hauck S., 1999, Stable isotopic studies of mafic sills and Proterozoic metasedimentary rocks located beneath the Duluth Complex, Minnesota: *Geochim. Cosmochim. Acta* **63**, 657-674.
- <sup>3</sup> Lee C.-T., Rudnick R. L., and Brimhall G. H. Jr. (2001) Deep lithospheric dynamics beneath the Sierra Nevada during the Mesozoic and Cenozoic as inferred from xenolith petrology. *Geochem. Geophys. Geosystems* **2**, 2001GC000152.
  - Lee C.-T., Rudnick R. L., McDonough W. F., and Horn I. (2000) Petrochemical investigation of carbonates in peridotite xenoliths from northeastern Tanzania. *Contrib. Mineral. Petrol.* **139**, 470-484.
- <sup>4</sup> Ussler W. III and Glazner A. F. (1992) Graphical analysis of enthalpy-composition diagrams in mixed magmas. *J. Volcanol. Geotherm. Res.* **51**, 23-40.
- <sup>5</sup> Herd C. D. K., Borg L. E., Jones J. H. and Papike J. J. (2002) Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. *Geochim. Cosmochim. Acta* **66**, 2025-2036.